

**Description of  
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Thermoplastic polymeric composition containing polyamide

The present invention relates to a thermoplastic polymeric composition containing polyamide, presenting an excellent compromise of properties, particularly of mechanical properties. The present composition in particular a substantial rigidity, a ductility or a substantial strength with the shock, and a satisfying behavior when it is subjected to relatively high temperatures.

Among the properties which one often seeks to control for a thermoplastic material intended to be formatted by the technical ones such as the injection, the injection-gas, extrusion, extrusion-blowing, one quotes rigidity, the strength with the shocks, the dimensional stability, in particular at relatively high temperature, the low withdrawal after shaper, the ability with the bringing in painting by different processes, the aspect of surface, the density. These properties can be controlled, in some limit, by the choice of polymeric or the addition to polymeric of composed of different natures. In this last case, one speaks about polymeric compositions. The choice of a material for a given application is generally guided by the level of performance required with respect to certain properties and by its cost. One always again seeks materials capable to answer a schedule of conditions in term of performance and/or cost. The polyamide is for example a material largely used, particularly in the field of automotive industry.

The polyamide is polymeric which is resistant chemically, which is stable at high temperatures and which can be blended with other types of polymeric in order to modifying the properties of them. One can for example improve his impact strength by adding polymeric elastomeric.

One knows the polymer mixtures including/understanding of polyamide and polyphenylene oxide (PO). These polymer mixtures present excellent mechanical properties, which make them adapt for example for the manufacture of parts of automotive bodywork. They are however expensive, so that one is interested in other polymer mixtures including/understanding of polyamide. They after present moreover one strong withdrawal shaper, and a not very satisfying aspect of surface. One thus seeks compositions which could present mechanical properties of the same order, in particular in term of rigidity and strength to the shocks, without presenting these disadvantages.

One knows the polymer mixtures including/understanding of polyamide and the Acrylonitrile-Butadiene-Styrene (ABS). In these mixtures, these two polymeric, incompatible, are generally compatibilisés by functions maleic anhydride, carried by ABS or another polymeric. The compositions containing polyamide and of ABS thus compatibilized present bonded properties at each compound. Document EP 648811 described for example a polymer mixture including/understanding of polyamide, the compatibilisant ABS, one made up of a polymeric Styrene-Maléimide grafted with maleic anhydride, an elastomer ethylene-propylene grafted with maleic anhydride. This mixture present an excellent strength with the shocks with low temperature, and a strength raised with the chemical products, which had with polyamide.

The aspect of surface and the peignability of the compositions containing polyamide and ABS are particularly appreciated. However the module of these compositions and the temperature of deformation under load are insufficient for many applications. The withdrawal after the shaper is as for him to a certain extent still too substantial.

One knows the use of plate nanoparticles, for example derived from montmorillonite, in order to modify the properties of polyamide. It for example was described that the montmorillonite introduction into polyamide could improve the temperature of deformation under load, and rigidity. The presence of montmorillonite induced no improvement of the strength to the shocks. Of general manner, this one rather tends to be deteriorated. As example, document WO 0009571 described a manufacturing process of perforated including/understanding polyamide and nanoparticles derived from the montmorillonite, for which the strength with the shocks of polyamide is not degraded.

This one remains insufficient.

Document WO 0031185 described of the compositions including/understanding of polyamide, an elastomer and nanoparticles. These compositions present insufficient properties. When the nanoparticles are used in quantity sufficient for substantially improving rigidity of the compositions it appears a transition ductilefragile with an insufficient behaviour to the shocks to the temperatures from use. Compositions including/understanding only polyamide, an elastomer, and nanoparticles present is a rigidity which could be satisfying with an insufficient strength with the shocks, that is to say a strength with the shocks which could be satisfying with an insufficient rigidity. The reduction relative in the induced strength with the shocks by the presence of the nanoparticles in a composition including/understanding of the nanoparticles and an elastomer is very substantial. These compositions present moreover one aspect of surface and a peignability which are not completely satisfying for certain applications.

The present invention with for object to propose a new polymeric composition, containing polyamide and of ABS, which present a compromise of properties improved, particularly in term of strength to the shocks, rigidity, temperature, deformation under load, withdrawal to the

moulding, aspect of surface and peignability.

For this purpose, the invention proposes a thermoplastic composition including/understanding the following compounds:

Composed a: thermoplastic polyamide

Composed b: copolymer including/understanding a rubber on which are grafted acrylonitrile and a selected compound styrenic among styrene and A-methyl-styrene, the copolymer including/understanding if necessary functional groupings of compatibilisation with polyamide,

Compound C: if necessary one or more compatibilizing agents between polyamide and the compound B, of which at least one includes/understands functional groupings of compatibilisation with polyamide

Composed D: if necessary an elastomeric compound

Composed E: lamellar inorganic particles presenting a great factor of form at 5, whose small dimension is less to 10 Nm.

The composition according to the invention can be obtained according to several processes of which some will be described more in detail subsequently. During these processes one implements, either during one single operation or during several operations the compounds A, B, E, optionally the compounds C and D, and same optionally still of other made up. These processes lead to the formation of a thermoplastic composition, being able to be shaper by conventional processes.

One precise that the compositions can comprise the other made up ones. It can act in particular of made up of stabilization, reinforcement, pigmentation, fireproofing, catalysis. They can also comprise inorganic loads, such as kaolin, wollastonite, talc, or fibres of reinforcement such as glass fibres or of. carbon. These other composed or loads or fibres can be introduced into the composition at the time of the steps of manufacture of this one or during the preparation of each made up A and/or B and/or C and/or D and/or E. The compositions according to the invention not including/understanding inorganic loads or fibres of reinforcement present a compromise between the mechanical density and properties particularly interesting: the material present a strength with the substantial shocks and a rigidity for a density which remains low.

The composition according to the present invention preferably a continuous phase of polyamide (compound A) in which are dispersed nodules including/understanding the compound B. For this purpose the composition preferably comprises more polyamide than of compound B. The polyamide and the compound B are not miscible. The dispersion of the compound B in polyamide is facilitated by the presence of functional groupings of compatibilisation with polyamide. These functional groupings can be carried by the compound B, or a compatibilizing agent, generally miscible with the compound B. The compatibilisation makes it possible to improve the behavior of the compositions.

The compound E is consisted of the plate inorganic particles presenting a great factor of form at

5 and whose small dimension is less to 10 Nm. By factor of form, one understands the relationship between largest dimension characteristic of the shape of the particles and smallest dimension characteristic of the shape of the particles. For plate particles, small dimension is the thickness. These particles are dispersed in the composition. Dispersion can be of more or less good quality: it is possible that the present composition of the plate agglomerates of particles. The particles are preferably dispersed in polyamide. It is however possible that particles present in the other ones are composed, for example in the compound B.

The particles, dispersed, constituting the compound E are generally obtained starting from a compound having a structure in layers. During the preparation of the composition the layers separate the ones the other ones for thus forming the particles. The small dimension of the particles is substantially that of a layer. The geometry of the particles, namely their forms and dimensions can be observed in the compositions by microscopy, or to be comparable with that of the layers of the compound from which they are obtained. As mentioned higher, it is possible that the separation of the layers is not total and that agglomerates are present in the composition.

One details now the different made up ones of the composition.

#### Composed A

Compound A is thermoplastic polyamide. It can be a question of only one polyamide or a mixture of several polyamides. In this last case, the mixture can either be obtained by an operation preceding the preparation by the composition, or to be obtained during the preparation of the composition by bringing in simultaneous or successive work of different polyamides.

The polyamide can be selected among: them polyamides of the type of those obtained starting from lactams eVou of amino-acids them polyamides of the type of those obtained starting from diacids and diamines - copolyamides of these two types of polyamides.

One particularly prefers polyamides chosen among polyamide 6, polyamide 11, polyamide 12, polyamide 4.6, polyamide 6.6, polyamide 6.10, polyamide 6.36, copolyamides 6/6. 6 and 6/6. 36, mixtures and copolymers containing these polyamides and copolyamides.

Compound A is preferably containing polyamide 6.6. It can be a question of single polyamide 6.6 or a polyamide 6 and polyamide 6.6 mixture. In the frame of such a mixture, the proportion in polyamide 6 weight compared to the total polyamide weight preferably is included/ understood between 1 and 30%.

The compositions containing polyamide 6.6 have excellent mechanical properties and excellent properties of strength at heat, and a substantial hardness. They are particularly adapt with the processes of bringing in painting by cataphoresis, which impose on material substantial temperatures.

The presence of polyamide 6 with polyamide 6.6 can particularly make it possible to reduce the withdrawal after shaper, to improve the compatibilisation between polyamide and the compound B and thus to improve certain mechanical properties.

According to a preferential characteristic, polyamide 6.6 used, single or in mixture, preferably includes/understands more final groupings amines than of final groupings acids. Such a characteristic improves the compatibilisation, the properties mechanical and/or the aspect of surface of the articles made up of the composition.

The quantity of final groupings amines is preferably great to 50 meq/kg and the difference between the quantities of final groupings amines and final groupings acids is preferably great to 5 meq/kg, even preferably great to 10 meq/kg. The quantities of final groupings amines and/or acids are determined by potentiometric proportionings after dissolution of polyamide. A method for example is described in " Encyclopedia off Industrial Chemical Analysis ", volume 17, page 293,1973.

### Compound B

The compound B is a copolymer including/understanding a rubber on which are grafted acrylonitrile and a selected styrenic compound among styrene and a-methylestyrene. This copolymer is thermoplastic. It can comprise in addition to the functional groupings intended to improve its compatibility with polyamide. The copolymer includes/understands preferably between 10 and 90% in rubber weight. The content of rubber of the whole of the compound B is preferably 15 to 35% in weight.

The rubber is preferably selected in the group consisted polybutadiene, the rubber butadiene-styrene, the rubber butadiene-acrylate, the rubber butadiene-acrylonitrile, the EPR (rubber of ethylene-propylene) and the EPDM (rubber of ethylene-propylene-diene) or of the mixtures of two or more than two of these rubbers.

The compound B can be prepared of the usual manner, for example by grafting of the monomers of the styrenic compound and acrylonitrile on the rubber. This can be carried out by polymerization in mass, solution or suspension. It is also possible to combine two or more than two of these methods of polymerization to realize, for example, polymerization in mass in solution, polymerization in mass in suspension or polymerization in emulsion-suspension.

Polymerization is preferably carried out in the presence of usual substances, such as the radical donors free ones, optionally in combination with a system redox, regulative agents of chain, stabilizing agents, of the agents of bringing in suspension, emulsifier and similar.

The compound B is preferably an Acrylonitrile-Butadiène copolymer Styrene. The content of butadiene weight in this compound for example lies between 15 and 35%, the content of styrene weight compared to the weight of styrene and of acrylonitrile

preferably is included/understood between 20 and 80%, preferably great to 50%. It can for example act of a copolymer Acrylonitrile-Butadiene-Styrene of which the proportions out of Acrylonitrile, Butadiène and Styrene are respectively approximately 25%, 25% and 50%.

According to an embodiment particular, the compound B includes/understands functional groupings of compatibilisation with polyamide. These groupings are preferably selected among the groupings maleic anhydride, carboxylic acid, ester. Such groupings for example are obtained by use of a comonomère during the preparation of the compound B, for example of maleic anhydride or acrylamide.

### Compound C

The compositions can comprise one or more compatibilizing agent between polyamide and the compound B. At least one of these agents includes/understands functional groupings of compatibilisation with polyamide. If it acts several agents, the mixture can either be obtained by an operation preceding the preparation by the composition, or to be obtained during the preparation of the composition by bringing in simultaneous or successive work of the different compatibilizing agents.

The functional groupings of compatibilisation present in at least one of the agents can be of comparable nature that those optionally present in the compound B. They are preferably selected among the groupings maleic anhydride, carboxylic acid, ester. Such groupings are derived from a comonomère used during the preparation of the compound C, for example of maleic anhydride.

According to the embodiment for which the compound B includes/understands groupings of accounting with polyamide, the compositions do not comprise preferably a compound C.

As compatibilizing agents, one quotes the copolymers Styrene-Maléimides grafted with functional groupings chosen among the carboxylic acids and anhydrides. By copolymer styrene-maléimide, one understands polymeric presenting patterns resulting from styrene and patterns maléimides of formula (I)

EMI7.1

in which R is selected among hydrogen, radical alkyls, radical aromatic the or arylaromatique one. R is for example a grouping phenyl. The pattern maléimide can for example be selected among N-phénylmaléimide, N (ométhylphényle maléimide), N (m-méthylphenyl maléimide), N (p-méthylphenyl maléimide). Such copolymers can for example be obtained by maleic anhydride and styrene copolymerization then partial reaction with an amine, for example aniline to form the patterns maléimide starting from the patterns anhydride. The patterns anhydrides not having reacted with the amine constitute the fonctionnalisation. Another process consists with copolymériser directly of styrene, the maléimide and maleic anhydride.

One particularly prefers as compatibilizing agent copolymers

Styrene-Maléimide grafted maleic anhydride, of which the proportions in weight of the different patterns are included/understood, between 40 and 60% of patterns styrene, between 40 and 60% of N-phénylmaléimide patterns, between 0,1 and 5% of patterns maleic anhydride. These copolymers have properties mechanical and thermal particularly high, which makes particularly the compositions powerful, in particular with regard to the properties evaluated at temperature relatively high.

The composition can include/understand also a copolymer Styrene-Maléimide not grafted.

As compatibilizing agent one quotes the copolymers block also

Fully or partially hydrogenated Styrene-Ethylene-Butadiene-styrene or Styrene-Butadiene-Styrene if necessary, presenting functional groupings of compatibilisation with polyamide, for example of the functional groupings maleic anhydride. Such compounds are known of the specialist of the profession. This type of copolymers for example is marketed by the Shell company under the Kraton range.

One quotes particularly the copolymer styrene-ethylene-butylene-styrene modified with maleic anhydride (SEBS-G-AM). The proportion in weight of this agent in the composition preferably lies between 0,5 and 10%. It is preferably less to 5%.

One can preferably use as compatibilizing agents at the same time

Styrene-Maléimide grafted maleic anhydride and of the SEBS grafted maleic anhydride.

One can also use as compatibilizing agent a copolymer styrene-acrylonitrile grafted maleic anhydride, or same of maleic anhydride introduces directly during the preparation of the composition.

#### Composed D

The compositions can comprise an elastomeric compound. Such compounds are generally used in order to modify the impact strength of the compositions. The proportion in weight of made up D in the composition is preferably less or equal to 50% in weight, even preferably less or equal to 10. According to a preferential characteristic of the invention this compound is grafted with functional groupings chosen among the carboxylic acids and anhydrides of acids. The grafting by anhydride of acid of copolymers is generally obtained by copolymerization in the presence of maleic anhydride.

The elastomers being able to be used as agents modifiers of impact strength are defined like having a tensile modulus ASTM D-638 less with approximately 40000, generally less with 25000, and preferably, less to 20000. They can be random, sequenced or grafted copolymers homopolymers. Polymeric the rubbery useful ones can be prepared starting from reactive monomers which can make part of the chains or ramifications of the polymeric one, or be grafted on the polymeric one. These reactive monomers can be dienes, carboxylic acids, and

their derivatives, such as esters and anhydrides. Among these polymeric rubbery, one will quote the polymeric ones of butadiene, butadiene copolymers/styrene, the isoprene, chloroprene, acrylonitrile copolymers/butadiene, isobutylene, copolymers of isobutylene-butadiene, ethylene copolymers/propylene (EPR), copolymers of ethylene/propylene/diene (EPDM).

Like polymeric rubbery useful, one can quote the polymeric ones obtained starting from aromatic vinyl monomers, of olefines, the acrylic acid, the methacrylic acid and their derivatives, and their salts metallic. Polymeric the rubbery useful ones are described in patents US-A-4315086 and US-A-4174358.

A first agent preferred modifier of impact strength for the realization of the invention is a functionalized copolymer which is a copolymer of ethylene and an other alpha-olefin than ethylene, having a functionality like a carboxyl or an anhydride, grafted on ethylene copolymer. The ethylene and the A-olefine are preferably a copolymer of ethylene and an A-olefine selected among an A-olefine at least in C3-C8, and preferably, in C3-C6. One prefers propylene like A-olefine monomer in C3-C8 in copolymer. Other A-olefines in C3-C6, such as 1-butylene, 1-pentene, and the 1-hexane, can be used with the place or in addition to propylene in copolymers. For the bringing in work of the invention according to a mode preferential, one can quote the rubbers ethylene-propylene grafted (functionalized) by maleic anhydride and the rubbers ethylene-propylene-dienes grafted (functionalized) by maleic anhydride.

#### Composed E

As mentioned higher, the particles, dispersed, constituting the compound E are generally obtained starting from a compound having a structure in layers.

During the preparation of the composition the layers separate the ones the other ones for thus forming the particles. The separation of the layers is often called exfoliation, dissociation and delamination. The processes which are brought into play during this separation can be different according to the compounds used and/or processes' used.

They lead to the obtaining of particles with more or less high factor of form whose small dimension is less to 10 Nm. Small dimension, for example the thickness of the particles is even preferably less to 2 Nm.

The compound with plate structure can be selected among several families. One quotes the fluoromicas, zirconium the phosphates, the silicates, particularly the phyllosilicates, hydrotalcites.

One quotes like suitable plate silicates for the bringing in work of the invention montmorillonites, smectites, illites, sepiolites, palygorkites, muscovites, Al, amesites, hectorites, talcs, fluorohectorites, saponites, beidellites, nontronites, stevensites, bentonites, the micas, fluoromicas, vermiculites, fluorovermicullites, halloysites. These compounds can be of natural



origin, synthetic, or natural modified. Montmorillonites particularly are preferred.

The separation of the layers in plates (exfoliation, dissociation...) can be supported by a prior treatment using an organic compound, for example an organic compound allowing to increase the distance between the layers. The nature of the treatment can depend on the nature made up to structure in layers. One quotes as examples the treatments by substituted ioniums, i.e. ammoniums or phosphoniums, for the treatment of montmorillonites. Already treated montmorillonites are available in the trade. Many treatments and/or processes of incorporation of composed with structure in layers in the thermoplastic ones, for example in polyamide, were described.

For the treatment of montmorillonites, and optionally of other composed with structure in layers, one quotes in particular the treatments by exchange of cations contained initially in the compound. It acts for example of organic cations of ioniums type. The organic cations can be selected among phosphoniums and ammoniums, for example primary ammoniums with quaternary. One can quote for example protonated amino acids such as the protonated acid 12-aminododecanoic out of ammonium, the primary amines with tertiary protonated and quaternary ammoniums.

The chains attached to the nitrogen atom or of phosphorus of onium can aliphatic, aromatic, arylaliphatic, linear or be connected and can present oxygenated patterns, for example patterns hydroxy or ethoxy. One can quote as example of organic treatments ammoniums the dodecyl ammonium, the octadecyl ammonium, bis (2-hydroxyethyl) the octadecyl methyl ammonium, the dimethyl dioctadecyl ammonium, the octadecyl benzyl dimethyl ammonium, the tetramethyl ammonium. One can quote as example of organic treatments phosphonium the alkyl phosphonium such as the tetrabutyl phosphonium, the trioctyl octadecyl phosphonium, the octadecyl triphenyl phosphonium. These lists do not have any restrictive character.

The silicates in suitable layers for the realization of the invention can be selected among montmorillonites, smectites, illites, sepiolites, palygorkites, muscovites, Al, amesites, hectorites, talcs, fluorohectorites, saponites, beidellites, nontronites, stevensites, bentonites, the micas, fluoromicas, vermiculites, fluoro-vermiculites, halloysites. These compounds can be of natural origin, synthetic, or natural modified.

According to an embodiment preferred of the invention, the compositions are made up of resin polyamide and plate particles dispersed in the resin, obtained by exfoliation of a phyllosilicate, for example a montmorillonite having previously undergone a treatment of swelling per exchange of ions. Examples of blowing treatments being able to be used for example are described in the patent

EP 0398551. All the known treatments to support the exfoliation of the phyllosilicates in a polymeric matrix can be used. One can for example use a treated clay by an organic compound marketed by the Laporte company under the Cloisite<sup>®</sup> mark. One can also use clays

containing montmorillonites marketed by the Nanocor Company under the Nanomer range.

Any method making it possible to obtain a dispersion of particles in polymeric can be used to implement the invention. A first process consists in mixing the compound with structure in layers to be dispersed, optionally treated for example by a blowing agent, in the polymeric molten one and with optionally subjecting the mixture to a substantial shearing, for example in a device of extrusion Bi-screw, in order to carry out a good dispersion. The polymeric one in question is heard either like one of the taken compounds individually, preferably of polyamide, or like the mixture of different composed of the composition. Another process consists in mixing the compound to be dispersed, optionally treated for example by a blowing agent, with the monomers in the polymerization medium, then to polymerize. In this case the polymeric one is preferably the polyamide. One thus introduces the plate compound optionally treated into a medium including/understanding of the polyamide monomers then one polymerizes in order to obtain a polyamide (compound A) including/understanding the compound E. Another process consists in mixing with polymeric molten a mixture concentrated of polymeric and particles dispersed, prepared for example according to one of the processes described previously.

The proportions in weights of different made up are preferably the following ones:

Composed a: between 5 and 95%, preferably between 30 and 70%

Composed b: between 5 and 95%, preferably between 20 and 40%

Compound C: between 0 and 30%, preferably between 5 and 20%

Composed D: between 0 and 30%, preferably between 1 and 10%

Composed E: between 0,1 and 30%, preferably between 1 and 10%

One details now processes being able to be used for the preparation of a composition according to the invention.

The thermoplastic compositions are generally obtained by mixture of the different compounds incoming in the composition, the thermoplastic compounds being in molten form. One proceeds to more or less high temperature, with more or less high force of shearing according to the nature of different made up. The compounds can be introduced simultaneously or successively. One generally uses a device of extrusion in which the material is heated, subjected to a force of shearing, and conveyed. Such devices are perfectly known of the specialist of the profession.

According to a first embodiment, one mixture all compounds in molten phase during a single operation, for example during an operation of extrusion. One can for example proceed to a mixture the granulated ones of polymeric materials, introduce them into the device of extrusion in order to melt them and to subject them to a more or less substantial shearing, and to introduce the compound E, or generally exactly a compound with plate structure forming treaty of the particles during the preparation of the composition. One prefers in the frame of such a process to operate under a relatively substantial shearing in order to support the dissociation of the plates.

One can, according to embodiments' particular, to carry out premixings of some of made up the

front preparation of the final composition.

According to an embodiment particular, the manufacturing process of the compositions according to the invention includes/understands the following operations: a) preparation of a composite material including/understanding of polyamide and the compound E b) phase mixture molten of composite material, other composed and if necessary of polyamide not including/understanding a compound E.

The prepared composite material with the step has) can be obtained by one of the following processes: - polymerization of polyamide in the presence of the made up E in the form of particles or of a compound with structure in layers optionally treated. In the frame of such a process, the polyamide thus prepared is preferably containing polyamide 6, the monomers being mainly selected among caprolactam and/or the 6-amino-caproic acid.

- phase mixture molten of polyamide and the made up E in the form of particles or a compound with structure in layers optionally treated. The mixture can be carried out using a device of extrusion, preferably with substantial shearing.

The composite material obtained with the step has) constitutes a premixing. It will be phase mixture molten with other composed during an operation b), for example using a device of extrusion, as described previously. During this operation b), one can add polyamide not including/understanding the compound E. The polyamide constituting compound A included/understood in the composition comes then from polyamide of composite material, and polyamide added at the time of the operation b).

The composition according to the invention, when it is prepared using a device of extrusion is preferably conditioned in the form of granulated.

It, or generally accurately the granulated ones, is intended to be shaper using processes implying a fusion for the obtaining of articles. The articles are thus consisted of the composition.

The use of the compositions according to the invention is particularly interesting in the frame of the manufacture of articles for automotive industry, in particular for the manufacture of parts of bodywork.

Other details or benefits of the invention will appear clearly within sight of the given examples below solely as an indication.

Composed used - Composed A1: Polyamide 66, of relative viscosity of 2,90, including/understanding 55 meq/kg grouping terminals amines and 40 meq/kg of final groupings acids, marketed by the company Rhodia Engineering Plastics under the reference Technyl 29 AP NH.

- Composed A2: Polyamide 6, of relative viscosity of 3,0, marketed by the company Hyosung Corporation under the reference Toplamid 1021.

- Composed B1: Copolymer Acrylonitrile-Butadiene-Styrene marketed by company BASF Korea under the reference Teriuran EHI-5.

- Composed B2: Copolymer Acrylonitrile-Butadiene-Styrene marketed by the Kumho company under the reference Kumho 795.

- Composed C1: Copolymer Styrene-Maleimide (N-phenylmaleimide) grafted maleic anhydride, including/understanding 46% in Styrene weight, 53% in weight of N-phenylmaleimide, 1% in maleic anhydride weight, marketed by the company Nipponese Shokubaï under reference PSX 0371.

- Composed C2: Hydrogenated Styrene-Ethylène-Butylene-styrene (SEBS) grafted maleic anhydride marketed by the Shell company under reference FG1901X - Composed D1: Elastomer Ethylene-Propylene grafted maleic anhydride marketed by the company Mitsui Chemical under reference MP 0620.

- Composed E1: Montmorillonite treated with the assistance methyl-dihydrogène-octadecyl ammonium.

Composed E2: Montmorillonite treated using a quaternary ammonium salt marketed by the company Southern Clay Corp. under reference SCPX 2086 - Composite 1: polyamide 6 matrix including/understanding 3,9% (rate of ash) in weight of dispersed montmorillonite nanoparticles, obtained by polymerization starting from a medium including/understanding of caprolactam and a montmorillonite having undergone a treatment the dodecanoïque acid ammonium.

- Composed F1: Lubricating, Carbon black, Nigrosine  
Preparation of the compositions

The compositions were prepared by phase mixture molten using an extrusion machine Bi-screw of the WERNER type and PFLEIDERER ZSK. The conditions of extrusion were the following ones: - Temperature: between 240 and 280 C - Number of revolutions: between 200 and 300 turns/min - Flow between 25 and 30 kg/heure

Two different processes were employed: - Process 1: mixture out of extrusion machine of each of made up - Process 2: mixture in extrusion of a composite including/understanding of polyamide and the plate particles.

## Evaluations

Different tests were carried out on the compositions: - Constrained with the threshold of plasticity according to standard ASTM D638, measured after conditioning of the test-tube at 23

C and a relative moisture of 50%.

- Elongation with the rupture according to standard ASTM D638, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

- Flexural modulus according to standard ASTM D790, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

- Constrained of inflection according to standard ASTM D790, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

- Strength with the Izod shocks notched according to the D256 standard, measured at 23 C, the dry state, under impacts of 3,2t and 6,4t.

- Temperature of deformation under load (HDT-Heat deflection temperature) according to the D648 standard, under load of 4,6 kgf/cm<sup>2</sup> and 18,5 kgf/cm<sup>2</sup> - Withdrawal with the moulding: report/ratio (length of the mould-size of the molded test-tube) L (length of the mould), for a test-tube ASTM of 200 mm long and of 3,2 mm thickness, measured lengths in the direction of injection of the test-tube.

Rockwell hardness according to standard ASTM D785.

Density according to standard ASTM D792

Constrained with the threshold of plasticity according to the standard ISO 527, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

Elongation with the rupture according to the standard ISO 527, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

Flexural modulus according to the standard ISO 178, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

Constrained of inflection according to the standard ISO 178, measured after conditioning of the test-tube at 23 C and a relative moisture of 50%.

Strength with the Izod shocks notched according to the standard ISO 180/1A, measured at 23 C, the dry state, under impacts of 3,2t and 6,4t.

Strength with the Charpy shocks notched according to the standard ISO 179/1eA, measured at 23 C, the dry state, under impacts of 3,2t and 6,4t.

Hardness Vicat A/120 according to the standard ISO 306.

Spiral test (fluidity with the molten state):

The compositions are shapers of granulated, which molten then are injected into a mould in the shape of spiral with rectangular section of thickness 2 mm and width 2.4 mm, in a press ENGEL 80T at a temperature of sleeve ranging between 240 and 260 C, with a pressure of injection 100 bars and a speed of injection of 60 m/s. The duration of injection is 5 seconds. The result is expressed in length of mould filled correctly by the composition. The compositions evaluated in this test have a content water front moulding of 0,1%.

Examples 1 to 4

The different compositions corresponding with the different examples (1,2,3,4) and comparative examples (C1, C2, C3, C4, C5) and the evaluations are presented in tables I and It.

Table #

EMI16.1

<Tb> Example <SEP> C1 <SEP> C2 <SEP> 1 <SEP> 2 <SEP> 3 <SEP> 4

<Tb> Composed <SEP> A1 <SEP> 67% <SEP> 54% <SEP> 56% <SEP> 53% <SEP> 49% <SEP> 47%

<Tb> Composed <SEP> A2 <SEP> 10% <SEP> 10% <SEP> 10% <SEP> 10% <SEP> 10%

<Tb> Composed <SEP> B1 <SEP> 15% <SEP> 20% <SEP> 20% <SEP> 20% <SEP> 20% <SEP> 20%

<Tb> Composed <SEP> C1 <SEP> 10% <SEP> 10% <SEP> 10% <SEP> 10% <SEP> 10% <SEP> 10%

<Tb> Composed <SEP> E1 <SEP> 3% <SEP> 3% <SEP> 5% <SEP> 5%

<Tb> Composed <SEP> D1 <SEP> 7% <SEP> 5% <SEP> 3% <SEP> 5% <SEP> 7%

<Tb> Composed <SEP> F1 <SEP> 1% <SEP> 1% <SEP> 1% <SEP> 1% <SEP> 1% <SEP> 1%

<Tb> Property <SEP> Test <SEP> Unit

<Tb> Constrained <SEP> in <SEP> tension <SEP> ASTM <SEP> Kg/cm<sup>2</sup> <SEP> 606 <SEP> 622 <SEP> 705 <SEP> 630 <SEP> 614 <SEP> 596

<Tb> with <the SEP> threshold <SEP> <SEP> plasticity <SEP> D638

<Tb> <SEP> Elongation <SEP> with <SEP> <the SEP> rupture <SEP> ASTM <SEP> % <SEP> 40 <SEP> 42 <SEP> 33 <SEP> 39 <SEP> 43 <SEP> 40

<Tb> <SEP> D638

<Tb> <SEP> Module <SEP> <SEP> inflection <SEP> ASTM <SEP> Kg/cmZ <SEP> 23610 <SEP> 23490 <SEP> 29720 <SEP> 27540 <SEP> 28540 <SEP> 27470

<Tb> <SEP> D790

<Tb> Constrained <SEP> in <SEP> inflection <SEP> ASTM <SEP> Kg/cm<sup>2</sup> <SEP> 921 <SEP> 910 <SEP> 1075 <SEP> 976 <SEP> 945 <SEP> 900

<Tb> <SEP> D790

<Tb> <SEP> Impact <SEP> Izod <SEP> notched <SEP> with <SEP> ASTM <SEP> Kgf.  
 <SEP> cm/c <SEP> 25,3 <SEP> 44,2 <SEP> 15,5 <SEP> 22,6 <SEP> 20,4 <SEP> 21, <SEP> 5  
 <Tb> 3.2t <SEP> D256 <SEP> m  
 <Tb> <SEP> Impact <SEP> Izod <SEP> notched <SEP> with <SEP> ASTM <SEP> Kgf.  
 <SEP> cm/c <SEP> 23,7 <SEP> 25,7 <SEP> 13,2 <SEP> 21,0 <SEP> 18,1 <SEP> 19,1  
 <Tb> 6,4t <SEP> D256 <SEP> m  
 <Tb> <SEP> H <SEP> DTà <SEP> 4.55 <SEP> kgf/cm <SEP> ASTM <SEP> C <SEP> 182,0  
 <SEP> 167,8 <SEP> 166,3 <SEP> 174,3 <SEP> 177,3 <SEP> 171, <SEP> 6  
 <Tb> <SEP> D648  
 <Tb> <SEP> HDT <SEP> &commat; <SEP> 18.5 <SEP> kgf/cm2 <SEP> ASTM <SEP> C  
 <SEP> 90, <SEP> 3 <SEP> 84, <SEP> 0 <SEP> 95,9 <SEP> 93, <SEP> 3 <SEP> 100, <SEP>  
 0 <SEP> 107,2  
 <Tb> <SEP> D648  
 <Tb> <SEP> Withdrawal <SEP> with <the SEP> moulding <SEP> REFERENCE MARK  
 <SEP> % <SEP> 1, <SEP> 57 <SEP> 1, <SEP> 41 <SEP> 1, <SEP> 16 <SEP> 1,24 <SEP> 0,  
 <SEP> 95 <SEP> 0, <SEP> 95  
 <Tb> <SEP> Korea  
 <Tb> Hardness <SEP> Rockwell <SEP> ASTM <SEP> R-scale <SEP> 116, <SEP> 0 <SEP>  
 116, <SEP> 2 <SEP> 118, <SEP> 3 <SEP> 116, <SEP> 6 <SEP> 114, <SEP> 8 <SEP> 113,  
 <SEP> 5  
 <Tb> <SEP> D785  
 <Tb> <SEP> Density <SEP> ASTM <SEP> g/cm'1, <SEP> 099 <SEP> 1,099 <SEP> 1,121  
 <SEP> 1,111 <SEP> 1,105 <SEP> 1, <SEP> 100  
 <Tb> <SEP> D792  
 <Tb> Constrained <SEP> in <SEP> tension <SEP> ISO <SEP> 527 <SEP> kJ/m'57, <SEP> 7  
 <SEP> 61,0 <SEP> 68, <SEP> 7 <SEP> 61,5 <SEP> 60,1 <SEP> 57,5  
 <Tb> with <the SEP> threshold <SEP> <SEP> plasticity  
 <Tb> Elongation <SEP> with <SEP> <the SEP> rupture <SEP> ISO <SEP> 527 <SEP> 46  
 <SEP> 67 <SEP> 35 <SEP> 50 <SEP> 40 <SEP> 36  
 <Tb> Module <SEP> <SEP> inflection <SEP> ISO <SEP> 178 <SEP> kJ/m'2351 <SEP> 2258  
 <SEP> 2818 <SEP> 2585 <SEP> 2735 <SEP> 2648  
 <Tb> Constrained <SEP> in <SEP> inflection <SEP> ISO <SEP> 178 <SEP> kJ/m <SEP> 86,  
 <SEP> 3 <SEP> 91, <SEP> 3 <SEP> 102, <SEP> 9 <SEP> 94, <SEP> 3 <SEP> 92, <SEP> 1  
 <SEP> 88, <SEP> 4  
 <Tb> <SEP> Impact <SEP> Izod <SEP> notched <SEP> ISO <SEP> N/mm2 <SEP> 9,7  
 <SEP> 8,8 <SEP> 6,7 <SEP> 9,7 <SEP> 1,6 <SEP> 15,1  
 <Tb> <SEP> 180/1A  
 <Tb> Impact <SEP> Charpy <SEP> notched <SEP> ISO <SEP> N/mm2 <SEP> 12, <SEP> 2  
 <SEP> 15,9 <SEP> 7, <SEP> 7 <SEP> 12,0 <SEP> 18,5 <SEP> 17,5  
 <Tb> <SEP> 179/1eA  
 <Tb> Hardness <SEP> Vicat <SEP> A/120 <SEP> ISO <SEP> 306 <SEP> 251, <SEP> 3  
 <SEP> 245,8  
 <Tb>

Table II  
EMI17.1

<Tb> Example <SEP> 4 <SEP> C3 <SEP> C4 <SEP> 5 <SEP> C5  
 <Tb> ComposéA1  
 <Tb> ComposéA2 <SEP> 100% <SEP> 70%  
 <Tb> ComposéB1 <SEP> 20% <SEP> 20% <SEP> 20%  
 <Tb> ComposéC2 <SEP> 2%  
 <Tb> ComposéC1 <SEP> 10% <SEP> 10% <SEP> 10%  
 <Tb> ComposéE1  
 <Tb> ComposéD1 <SEP> 5%  
 <Tb> Composite <SEP> 1 <SEP> 70% <SEP> 100% <SEP> 63%  
 <Tb> ComposéF1  
 <Tb> Property <SEP> Test <SEP> Unit  
 <Tb> Constrained <SEP> in <SEP> tension <SEP> ASTM <SEP> Kg/cm<sup>2</sup> <SEP> 801 <SEP> 1003 <SEP> 760 <SEP> 654 <SEP> 721  
 <Tb> with <the SEP> threshold <SEP> <SEP> plasticity <SEP> D638  
 <Tb> Elongation <SEP> with <SEP> <the SEP> rupture <SEP> ASTM <SEP> % <SEP> 22 <SEP> 2,6 <SEP> 150 <SEP> 47 <SEP> 53  
 <Tb> <SEP> D638  
 <Tb> Module <SEP> <SEP> inflection <SEP> ASTM <SEP> kg/cm<sup>3</sup>6450 <SEP> 43350  
 <SEP> 25500 <SEP> 29360 <SEP> 25440  
 <Tb> <SEP> D790  
 <Tb> Constrained <SEP> in <SEP> inflection <SEP> ASTM <SEP> kg/cm<sup>3</sup>1264 <SEP> 1576  
 <SEP> 1000 <SEP> 998 <SEP> 1058  
 <Tb> <SEP> D790  
 <Tb> Impact <SEP> Izod <SEP> notched <SEP> with <SEP> ASTM <SEP> kgf. <SEP> cm/c  
 <SEP> 12,3 <SEP> 5,5 <SEP> 5,5 <SEP> 53,5 <SEP> 13,8  
 <Tb> 3.2t <SEP> D256 <SEP> m  
 <Tb> Impact <SEP> Izod <SEP> notched <SEP> with <SEP> ASTM <SEP> kgf. <SEP> cm/c  
 <SEP> 13,6 <SEP> 4,0 <SEP> 4,5 <SEP> 27,2 <SEP> 10,9  
 <Tb> 6.4t <SEP> D256 <SEP> m  
 <Tb> HDTà <SEP> 4. <SEP> 55 <SEP> kg/cm<sup>3</sup> ASTM <SEP> C <SEP> 172,5 <SEP> 196,3  
 <SEP> 170 <SEP> 151,7 <SEP> 141,6  
 <Tb> <SEP> D648  
 <Tb> HDT <SEP> &commat; <SEP> 18.5 <SEP> kg/cm<sup>2</sup> <SEP> ASTM <SEP> C <SEP> 101,8 <SEP> 145,6 <SEP> 65 <SEP> 107,6 <SEP> 75,8  
 <Tb> <SEP> D648  
 <Tb> Withdrawal <SEP> with <the SEP> moulding <SEP> REFERENCE MARK <SEP> %  
 <SEP> 0,78 <SEP> 1,02 <SEP> 1,28 <SEP> 0,82 <SEP> 0,76  
 <Tb> <SEP> Korea  
 <Tb> Hardness <SEP> Rockwell <SEP> ASTM <SEP> R-scale <SEP> 120 <SEP> 119,



<SEP> 5 <SEP> 120 <SEP> 116, <SEP> 7 <SEP> 119,5

<Tb> <SEP> D785

<Tb> Density <SEP> ASTM <SEP> g/cm<sup>3</sup>, <SEP> 124 <SEP> 1,144 <SEP> 1, <SEP> 14  
<SEP> 1,102 <SEP> 1, <SEP> 106

<Tb> <SEP> D792

<Tb> Constrained <SEP> in <SEP> tension <SEP> ISO <SEP> 527 <SEP> kJ/m <SEP> 79,  
<SEP> 5 <SEP> 102,1 <SEP> 78 <SEP> 64,7 <SEP> 69,5

<Tb> with <the SEP> threshold <SEP> <SEP> plasticity

<Tb> Elongation <SEP> with <SEP> SEP <has> rupture <SEP> ISO <SEP> 527 <SEP> %  
<SEP> 18 <SEP> 2,6 <SEP> 100 <SEP> 42 <SEP> 48

<Tb> Module <SEP> <SEP> inflection <SEP> ISO <SEP> 178 <SEP> kJ/m<sup>2</sup> <SEP> 3550  
<SEP> 4251 <SEP> 2600 <SEP> 2875 <SEP> 2448

<Tb> Constrained <SEP> in <SEP> inflection <SEP> ISO <SEP> 178 <SEP> kJ/m<sup>2</sup> <SEP>  
1256 <SEP> 150,2 <SEP> 105 <SEP> 98,2 <SEP> 98,6

<Tb> Impact <SEP> Izod <SEP> notched <SEP> ISO <SEP> N/mm<sup>2</sup> <SEP> 7,8 <SEP> 4,8  
<SEP> 4,7 <SEP> 42,7 <SEP> 7,2

<Tb> <SEP> 180/1A

<Tb> Impact <SEP> Charpy <SEP> notched <SEP> ISO <SEP> N/m<sup>9</sup>, <SEP> 5 <SEP> 6,7  
<SEP> 5,5 <SEP> 45,5 <SEP> 8,5

<Tb> <SEP> 179/1eA

<Tb> <SEP> ISO <SEP> 306 <SEP> C <SEP> 204,8 <SEP> 213, <SEP> 3 <SEP> 214 <SEP>  
203,5 <SEP> 205, <SEP> 2

<Tb>

#### Example 5

The prepared compositions are presented in table III

Table III

EMI18.1

<Tb> Example <SEP> 5 <SEP> C6

<Tb> <SEP> (comparative)

<Tb> Composed <SEP> A2 <SEP> 53% <SEP> 53%

<Tb> Composed <SEP> B2 <SEP> 30% <SEP> 32%

<Tb> Composed <SEP> C1 <SEP> 10% <SEP> 10%

<Tb> Composed <SEP> D1 <SEP> 5% <SEP> 5%

<Tb> Composed <SEP> E2 <SEP> 2%

<Tb>

The evaluations of these compositions are presented in table IV

Table IV

EMI18.2

<Tb> <SEP> Example

<Tb> <SEP> Property <SEP> Test <SEP> Unit <SEP> 5 <SEP> C6  
 <Tb> <SEP> Density <SEP> ASTM <SEP> 1. <SEP> 0831 <SEP> 1.0835  
 <Tb> <SEP> D792  
 <Tb> <SEP> Constrained <SEP> in <SEP> tension <SEP> ASTM <SEP> kgf/cm'550. <SEP>  
 5 <SEP> 531. <SEP> 2  
 <Tb> with <the SEP> threshold <SEP> <SEP> plasticity <SEP> D638  
 <Tb> <SEP> Module <SEP> <SEP> inflection <SEP> ASTM <SEP> kgf/cm2 <SEP> 24330  
 <SEP> 21450  
 <Tb> <SEP> D790  
 <Tb> Constrained <SEP> in <SEP> inflection <SEP> ASTM <SEP> kgf/cm2 <SEP> 859.  
 <SEP> 7 <SEP> 812.3  
 <Tb> <SEP> D790  
 <Tb> <SEP> Impact <SEP> Izod <SEP> notched <SEP> with <SEP> ASTM <SEP> kgf.  
 <SEP> cm/cm <SEP> 84.67 <SEP> 77.2  
 <Tb> 3.2t <SEP> D256  
 <Tb> <SEP> Impact <SEP> Izod <SEP> notched <SEP> with <SEP> ASTM <SEP> kgf.  
 <SEP> cm/cm <SEP> 37.7 <SEP> 26.84  
 <Tb> 6.4t <SEP> D256  
 <Tb> <SEP> Hardness <SEP> Rockwell <SEP> ASTM <SEP> R-scale <SEP> 113.9 <SEP>  
 115.1  
 <Tb> <SEP> D785  
 <Tb> <SEP> HDT <SEP> with <SEP> 4. <SEP> 55 <SEP> kgf/cm <SEP> ASTM <SEP> C  
 <SEP> 131.7 <SEP> 128.2  
 <Tb> <SEP> D648  
 <Tb> HDTà <SEP> 18. <SEP> 5 <SEP> kgf/cm' ASTM <SEP> C <SEP> 109.1 <SEP> 103.  
 <SEP> 6  
 <Tb> <SEP> D648  
 <Tb> Length <SEP> spiral <SEP> cm <SEP> 325 <SEP> 235  
 <Tb>

Composition including/understanding of montmorillonites the present a fluidity into molten  
 higher than a composition not including/understanding montmorillonites, while presenting  
 similar mechanical properties.

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## Result Page

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**CLAIMS** 1. Thermoplastic composition including/understanding the following compounds:

Composed a: thermoplastic polyamide

Composed b: copolymer including/understanding a rubber on which are grafted acrylonitrile and a selected compound styrenic among styrene and A-methyl-styrene, the copolymer including/understanding if necessary functional groupings of compatibilisation with polyamide, Compound C: if necessary one or more compatibilizing agent between polyamide and the compound B, of which at least one includes/understands functional groupings of compatibilisation with polyamide

Composed D: if necessary an elastomeric compound

Composed E: lamellar inorganic particles presenting a great factor of form at 5 whose small dimension is less to 10 Nm.

2. Composition according to claim 1 characterized in that the polyamide constitutes a matrix inside which are dispersed nodules of the compound B.

3. Composition according to one of the preceding claims characterized in that the lamellar particles are dispersed in polyamide and if necessary in the compound B.

4. Composition according to one of the preceding claims characterized in that the compound B is a copolymer containing Acrylonitrile-Butadiene-Styrene, including/understanding if necessary functions of compatibilisation with polyamide 5. Composition according to one of the preceding claims characterized in that the compound C is selected among the copolymers styrene-maleimide including/understanding of the functional groupings of compatibilisation with polyamide, the copolymers block fully or partially hydrogenated Styrene-Ethylene-Butadiene-Styrene or Styrene-Butadiene-Styrene if necessary, presenting functional groupings of compatibilisation with polyamide.

6. Composition according to one of the preceding claims characterized in that the functional groupings of compatibilisation with polyamide are selected among the groupings maleic anhydride, carboxylic acid, ester.

7. Composition according to one of the preceding claims characterized in that the polyamide is selected among polyamide 6, polyamide 66, the mixtures and copolymers containing these polyamides.

8. Composition according to claim 8 characterized in that compound A is a polyamide 6 and polyamide 66 mixture, including/understanding between 1% and 30% of polyamide 6 compared to the total polyamide weight.

9. Composition according to one of the claims 7 or 8 characterized in that polyamide 66 includes/understands more final groupings amines than of final groupings acids.

10. Composition according to claim 9 characterized in that the quantity of final groupings amines is great to 50 meq/kg and in what the difference between the quantities of final groupings amines and final groupings acids is great to 5 meq/kg.

11. Composition according to one of the preceding claims characterized in that the plate inorganic particles are obtained starting from compounds having a structure in layers chosen among silicates, the fluoromicas, zirconium the phosphates, hydrotalcites.

12. Composition according to claim 11 characterized in that the plate particles are obtained starting from montmorillonite or from a compound derived from montmorillonite.

13. Composition according to claim 12 characterized in that the plate particles are obtained starting from montmorillonite treated by an agent drawing aside the layers.

14. Composition according to one of the preceding claims characterized in that the proportions in weights of different made up are the following ones:

Composed a: between 5 and 95%

Composed b: between 5 and 95%

Compound C: between 0 and 30%

Composed D: between 0 and 30%

Composed E: between 0,1 and 30% 15. Composition according to one of the preceding claims characterized in that the proportions in weights of different made up are the following ones:

Composed a: between 30 to 70%

Composed b: between 20 and 40%

Compound C: between 5 and 20%

Composed D: between 1 and 10%

Composed E: between 1 and 10% 16. Composition according to one of the preceding claims characterized in that the compound D is selected among the rubber Ethylene-Propylene grafted by maleic anhydride.

17. Manufacturing process of a composition according to one of the preceding claims

characterized in that it consists in mixing the compounds in molten phase.

18. Manufacturing process of a composition according to one of claims 1 to 16, characterized in that it includes/understands the following operations: a) preparation of a composite material including/understanding of polyamide and the compound E b) phase mixture molten of composite material, other composed and if necessary of polyamide not including/understanding a compound E.

19. Proceeded according to claim 18 characterized in that the composite material is prepared by one of the following processes: - polymerization of polyamide in the presence of the made up E in the form of particles or of a compound with structure in layers capable to generate the plate particles - phase mixture molten of polyamide and the made up E in the form of particles or a compound with structure in layers capable to generate the plate particles 20. Articles formatted made up of a composition according to one of the preceding claims.

21. Use of a composition according to one of claims 1 to 19 for the manufacture of parts of automotive bodywork.